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Final Report

IGNITION AND COMBUSTION OF LIQUID PROPELLANTS

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For consideration by
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January 15, 1990

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Introduction

A class of liquid propellants (LP) has been proposed for the launching of gun ordinances. These propellants are composed of salts of hydroxylammonium nitrate (HAN) with the formula NH_2OHNO_3 and aliphatic ammonium nitrate (AAN) dissolved in water. Although HAN and AAN are monopropellants themselves in that they contain both oxidizing and reducing elements, HAN, being oxygen rich based on $\text{N}_2\text{-H}_2\text{O}$ stoichiometry, can be considered to be the oxidizer of the system while AAN, being oxygen deficient, is the corresponding fuel.

Very little is known about the combustion characteristics of these liquid propellants. Operationally, the propellant is sprayed into the combustion chamber upstream of the gun barrel, ignites, and burns. The attendant pressure buildup provides the needed propulsive power for the ordnance. It is clear that droplet and spray processes are of central importance to the gun performance.

The present program is concerned with the gasification of single droplets of liquid propellants in controlled environments. Quantitatively, the most important parameter is the rate with which these droplets are gasified. This rate is determined by the regression rate of the droplet as well as the occurrence of a microexplosion phenomenon, characterized by the catastrophic fragmentation of the droplet. Obviously, liquid gasification is facilitated by advancing the onset of this event. Thus a particular focus of the present program is to quantify the overall droplet gasification rate, to understand the characteristics of, and the mechanisms controlling, microexplosion, and to explore means to facilitate its occurrence.

The research program has made worthwhile contributions in five areas, namely: (1) Determination of the droplet temperature at microexplosion, (2)

studies of droplet gasification under atmospheric pressure, (3) design and fabrication of a high-pressure droplet combustion chamber and an associated sampling probe, (4) studies of droplet gasification under elevated pressures, and (5) preliminary studies of the reaction mechanisms of the liquid propellants. Highlights of these results will be presented in the next section.

Summary of Accomplishments

All the experimental results to be reported in the following were obtained with an LP coded 1345, which consists of 63.2% HAN, 20.0% triethanolammonium nitrate (TEAN) and 16.8% water, all by weight. The specific concentrations of HAN and TEAN are such that they are in stoichiometric proportion according to



This LP has a heating value of about 1.0 kJ/g and calculated adiabatic flame temperature of 2285K. Tests were conducted with various amount of water addition to this LP.

1. LP Explosion Temperatures

An important information concerning LP combustion is the temperature range within which the liquid-phase reaction is initiated. This temperature has been reported to be around 120°C to 150°C for various HAN-based propellants. For the present HAN-TEAN mixture, we have found that this temperature is about 155°C when the sample is heated in containers of either metal or glass.

It is felt, however, that in these tests the presence of solid surfaces could interfere with the initiation of the liquid-phase reaction. In order to totally eliminate solid surfaces, the following experiment was performed. Here a propellant droplet of about 0.5 mm was introduced at the bottom of a heated column of host liquid which is immiscible with the propellant. The column was heated in such a way that a positive temperature gradient was established in the upward direction. The droplet rose due to buoyancy,

although the rise was sufficiently slow and the droplet size sufficiently small that the droplet was in perpetual thermal equilibrium with the host fluid. Thus when the droplet exploded upon reaching a certain height, the propellant explosion temperature should correspond to that of the host fluid at that location. Experiments were conducted for droplets of HAN/water, TEAN/water, and 1845, with various amounts of water dilution.

The host fluid used was a perfluoroalkylpolyether oil with the trade name Krytox 143AD, manufactured by Dupont Co. It has a density of 1.90 gm/cm^3 at 25°C and 1.60 gm/cm^3 at 200°C , and therefore is able to provide the needed buoyancy to the propellant whose density is 1.5 gm/cm^3 at 25°C .

The experimental results provide the following insight into the explosion mechanism of the liquid propellant. It seems that the explosion of LP-1845 is induced by liquid-phase chemical reactions instead of the homogeneous nucleation of water. Furthermore, these reactions are initiated by HAN because its explosion temperature closely follows that of LP-1845. As the extent of water dilution is increased, chemical reactivity is continually weakened until the explosion mechanism shifts to that of homogeneous nucleation of water.

A useful piece of information which also emerges from the above results is that the reaction temperature of LP-1845 is in the range of $200\text{--}230^\circ\text{C}$, and therefore is substantially higher than the previously reported values.

This work has been reported in Publication No. 1

2. Droplet Combustion under Atmospheric Pressure

In this experimental investigation a steady stream of droplets of equal size and spacing is downwardly and coaxially injected into the postcombustion

region of a flat flame, whose stoichiometry can be varied to achieve the desired temperature and oxidizer concentration in its downstream flow in which the droplets gasify. The instantaneous droplet image and size can be stroboscopically frozen and photographically recorded, while its corresponding composition can be determined through sampling. Before entering the sampling probe, the droplets are subjected to a gentle blowing of N_2 , which disperses the vapor around the droplets so that only the droplets constitute the collected sample; the dispersed vapor turns out to be negligible. For the present runs the ambient temperature is about $900^\circ C$.

The experiments yield the following insight regarding the droplet gasification mechanism. Upon exposure to the hot environment, whether it is oxidizing or inert, the droplet is first heated up and suffers very little mass loss. The period of heating depends on the droplet size while the extent of heating depends on the salt concentration. Thus the higher the salt concentration, the higher the droplet temperature will reach before this period of active droplet heating is over.

Active droplet gasification follows active droplet heating. The gasification rate constants of the propellants are found to be close to that of pure water, and suggest that water is the dominant gasifying species. The salts, however, are nevertheless also gasified to a certain extent because of the presence of an orange coloration surrounding the droplet when the environment is oxidizing. Mild liquid-phase reactions could also be taking place because of the somewhat substantial dependence of K on the initial droplet size.

The preferential gasification of water will lead to the gradual concentration of salt in the droplet. The efficiency and extent with which

salt is concentrated depends on the diffusional resistance experienced by the salt in the solution. The present data seem to suggest that the diffusional resistance may not be too strong, for two reasons. First, if diffusional resistance were strong, the gasification rate would have a much stronger dependence on the salt concentration, contrary to the observation. Second, the gasification rates of the LP droplets are between 0.14 and 0.18 mm²/s, which are substantially lower than the value of about 1 mm²/s for miscible hydrocarbon droplets. These lower gasification rates allow a longer time for the salt to diffuse.

With salt being continuously concentrated, a critical concentration corresponding to an average droplet density of 1.5 g/cm³ can be eventually reached, at which liquid-phase reaction is rapidly accelerated to cause droplet microexplosion. For mixtures with high initial water contents, it is possible that this critical density cannot be reached because during droplet gasification salt is still being depleted from the droplet composition to a certain extent. For these mixtures microexplosion does not occur.

Results from this study were reported in Publication No. 1.

3. Design and Fabrication of High Pressure Droplet Combustion Chamber

In order to conduct the high pressure experiments to be described in the next section, a high temperature, elevated-pressure (up to 5 atmospheres) droplet combustion chamber was designed, fabricated, and debugged. The basic operational principle of the apparatus is similar to that of the atmospheric combustor discussed in the previous section, although the specific requirement of elevated pressure and closed system renders the present apparatus a unique facility for the study of high-pressure droplet combustion.

Together with the high-pressure burner, a high-pressure sampling probe has also been designed, fabricated, and debugged. This probe allows the in-situ sampling of the droplets during different stages in their lifetimes, and consequently the study of the variation of droplet composition due to liquid-phase reaction.

4. Droplet Combustion under Elevated Pressures

There are two motivations for studying droplet combustion under elevated pressures. The first is that the interior gun environment has exceedingly high pressures. Thus studies of the droplet behavior with pressure variations should provide some insight into the effect of pressure. Second, since we have demonstrated the importance of liquid-phase reactions in LP droplet combustion, it is of interest to explore means to facilitate the droplet gasification rate by increasing the liquid-phase reaction rate. An obvious approach is to increase the droplet temperature. This can be achieved by increasing the system pressure and thereby the boiling point of the liquid.

Our experimental results have conclusively demonstrated that increasing pressure increases the droplet gasification rate as well as advances the onset of droplet microexplosion. For example, as the pressure increases from 1 to 3.5 atm., the droplet gasification rate constant increases from 0.08 mm²/s to 0.13mm²/s, while the droplet microexplosion diameter, normalized by its initial diameter, is advanced from 0.8 to 0.94 under the present experimental condition.

Results from this study were reported in Publication No. 4.

5. Chemical Analysis

In this project thermal decomposition of HAN, TEAN and liquid propellant 1845 have been studied using a variety of thermoanalytical instruments. The products were analyzed using infrared spectroscopy, nuclear magnetic resonance spectroscopy, gas chromatography and mass spectrometry. Our results on both solid HAN and TEAN suggest that a proton transfer is the first step in the thermal decomposition of HAN and TEAN. HAN decomposes much more exothermically at a lower temperature than TEAN. While the decomposition mechanism of HAN is much simpler, TEAN undergoes several chemical structural transformations giving rise to decomposition products such as 4-morpholine ethanol, 2,2'-(methylinino) bis-ethanol, 2,2',2"-nitrilotris-ethanol along with evolution of H_2O , CO_2 , and NO_2 . Our results also suggest that decomposition of TEAN occurs in an identical manner at both atmospheric and high pressures (800 psi).

List of Publications

- 1.* "Aerothermochemical Studies of Energetic Liquid Materials; 1. Combustion of HAN-Based Liquid Gun Propellants under Atmospheric Pressure," by D.L. Zhu and C.K. Law, Combustion and Flame, Vol.70, pp.333-342, (1987).
2. "Liquid-Phase Diffusional Resistance in Multicomponent Droplet Gasification," by A.L. Randolph, A. Makino, and C.K. Law, Twenty-First Combustion Symposium, the Combustion Institute, Pittsburgh, PA, pp.601-608, (1988).
3. "Time-Resolved Gasification and Sooting Characteristics of Droplets of Alcohol/Oil Blends and Water/Oil Emulsions," by A.L. Randolph and C.K. Law, Twenty-First Combustion Symposium, the Combustion Institute, Pittsburgh, PA, pp.1125-1130, (1988).
- 4.+ "Combustion and Microexplosion of HAN-Based Liquid Gun Propellants under Elevated Pressures," by C. Call, D.L. Zhu, S.C. Deevi, and C.K. Law, Paper No. 88-41, 1988 Spring Tech. Meeting of the Western States Section of the Combustion Institute, Salt Lake City, Utah, 1988.
5. "Dynamics of Stretched Flames," by C.K. Law, Twenty-Second Combustion Symposium, the Combustion Institute, Pittsburgh, PA, pp.1381-1402, (1989).
6. "Effect of Pressure on the Microexplosion of Water/Oil Emulsion Droplets over a Hot Plate," by P. Cho, C.K. Law, and M. Mizomoto, submitted.
7. "Some Recent Advances in Droplet Combustion," by C.K. Law, to appear in Proc. of the Third International Colloquium on Drops and Bubbles.

* Attached as Appendix A

+ Attached as Appendix B

List of Participants

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Aerothermochemical Studies of Energetic Liquid Materials: 1. Combustion of HAN-Based Liquid Gun Propellants Under Atmospheric Pressure

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The gasification and microexplosion characteristics of droplets of liquid gun propellants under atmospheric pressure have been experimentally investigated. Results show that the propellant explosion temperature is around 200°C and is substantially in excess of previously reported values. The droplet surface regression rate prior to the onset of microexplosion is found to be close to that of water and therefore is insensitive to the water content in the propellant as well as the oxygen concentration in the hot environment; these results demonstrate the dominance of water in the gasification process. It has also been determined that the propellant density attains a critical value of about 1.5 g/cm³ at the state of microexplosion.

1. INTRODUCTION

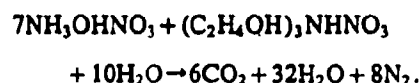
A class of liquid propellants (LP) has been proposed for the launching of gun ordnances [1, 2]. These propellants are composed of salts of hydroxylammonium nitrate (HAN) with the formula NH_2OHNO_2 and aliphatic ammonium nitrate (AAN) dissolved in water. Although HAN and AAN are monopropellants themselves in that they contain both oxidizing and reducing elements, HAN, being oxygen rich based on $\text{N}_2\text{-H}_2\text{O}$ stoichiometry, can be considered to be the oxidizer of the system while AAN, being oxygen deficient, is the corresponding fuel.

Very little is known about the combustion characteristics of these liquid propellants. Operationally, the propellant is sprayed into the combustion chamber upstream of the gun barrel, ignites, and burns. The attendant pressure buildup provides the needed propulsive power for the ordnance. It is clear that droplet and spray processes are of central importance to the gun performance.

The present paper reports our recent experimental data on the gasification and microexplosion

characteristics of LP droplets under atmospheric pressure. Specifically, we have determined the liquid temperature at which the droplet catastrophically ruptures, the droplet gasification rate prior to this microexplosion event, and the droplet size and density at microexplosion. These results provide useful insight into the combustion characteristics of this class of liquid propellants.

All the experimental results to be reported in the following were obtained with an LP coded 1845, which consists of 63.2% HAN, 20.0% triethanolammonium nitrate (TEAN) with the formula $(\text{C}_2\text{H}_4\text{OH})_3\text{NHNO}_2$, and 16.8% water, all by weight. The specific concentrations of HAN and TEAN are such that they are in stoichiometric proportion according to



This LP has a heating value of about 1.0 kJ/g and a calculated adiabatic flame temperature of 2285K. Tests were conducted with various amount of water addition to this LP.

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2. LP EXPLOSION TEMPERATURES

An important piece of information concerning LP combustion is the temperature range within which the liquid-phase reaction is initiated. This temperature has been reported to be around 120–150°C for various HAN-based propellants [1] when tested in closed pressure vessels undergoing slow heating. For the present HAN/TEAN mixture, we have found that this temperature is about 150°C when the sample is slowly heated in containers of either metal or glass.

It is felt, however, that the above test procedure could contain several sources of uncertainty which require further investigation. First, the samples were in contact with solid surfaces which could have some influence on the initiation kinetics of the reactions. Second, during such tests some water could have been vaporized when reaction was initiated, implying that the salt concentration might have changed from the original value. Third, the heating rate was much lower than what the LP droplets would experience in practical situations.

In order either to minimize or to eliminate these effects, the following experiment, schematized in Fig. 1, was performed. Here a propellant droplet of about 0.5 mm was introduced at the bottom of a

heated column of a host liquid which is immiscible with the propellant. The column was heated in such a way that a positive temperature gradient was established in the upward direction. The droplet rises fairly rapidly due to buoyancy, although the rise is still sufficiently slow and the droplet size is sufficiently small that the droplet can be considered to be in perpetual thermal equilibrium with the host fluid. Thus, when the droplet explodes upon reaching a certain height, the propellant explosion temperature should correspond to that of the host fluid at that location. The host fluid used was a perfluoroalkylpolyether oil with the tradename Krytox 143AD, manufactured by Dupont Co. It has a density of 1.90 g/cm³ at 25°C and 1.60 g/cm³ at 200°C, and therefore is able to provide the needed buoyancy to the propellant whose density is 1.45 g/cm³ at 25°C. It may be noted that this heated column method is an established technique for the determination of the limit of superheat of liquids [3]. We have also validated our apparatus and test procedure by determining the limits of superheat of various pure liquids—e.g., n-alkanes—and noting that they agree with published values to within 0.1–0.2°C.

With the present experimental arrangement, effects of solid surfaces and preexplosion vaporization can be considered to be eliminated. Concern-

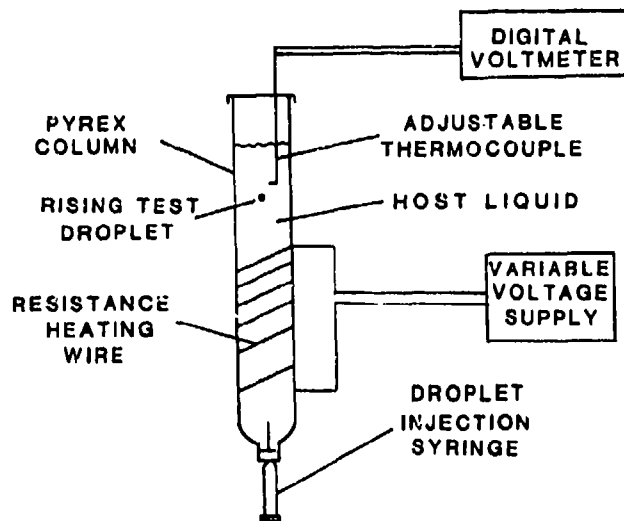


Fig. 1. Schematic of the apparatus used to determine the explosion temperature of the liquid propellant.

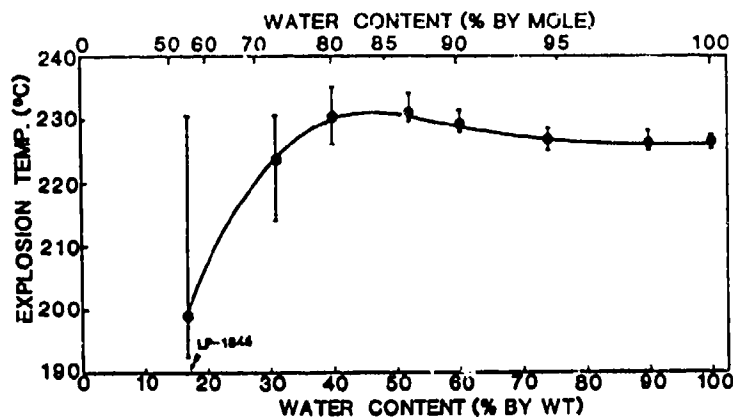


Fig. 2. Explosion temperature of HAN/TEAN mixture with various amounts of water dilution.

ing the liquid heating rate, in the present experiments it typically takes about 2–5 s for the droplet to rise to the explosion location. During this time the droplet temperature has increased from the room temperature to, say, 230°C (see Fig. 2). Thus the droplet experiences an average heating rate of about 10^2 °C/s. We have also determined that the present results are not affected by changing the heating rate by a factor of two or three, which is the flexibility we have in the present experimental arrangement. In the experiment of Ref. [1], the liquid is slowly heated from room temperature to, say, 150°C, in about 20 min, implying a heating rate of 10^{-1} °C/s. Thus the present heating rate is 10^3 times faster than that of Ref. [1].

For droplets of much smaller sizes which are of relevance in practical situations, the heating rate should be even higher. For example, Fig. 5 shows that a 100 μ m droplet takes about 75 ms to explode. Assuming the explosion temperature is around 230°C, then the droplet experiences a heating rate of about 3×10^3 °C/s. Since even a 100 μ m droplet is considered to be quite large within the spray interior, it is reasonable to assign a value of 10^4 °C/s as an average droplet heating rate in sprays. Thus our heating rate is still smaller than actual values by a factor of 10^2 . The influence of this heating rate difference on the actual droplet explosion behavior is not clear. Obviously if the mechanism responsible for drop-

let explosion has a rate which is much faster than the fastest heating rate, then droplet explosion is not expected to be affected much by the actual heating rate. On the other hand, for smaller explosion rates, a faster heating rate would allow the droplet to be heated to higher temperatures before droplet explosion takes place.

Figure 2 shows the explosion temperatures of the HAN/TEAN mixture with various extents of water dilution. The spread in the data represents the temperature range within which explosions have been observed to occur, with the data point itself representing the average of the temperatures at which over 90% of the explosion events occur. The results show that the spread is most severe for the solution with the highest salt content, namely, LP-1845. As the water content increases, the spread decreases while the most probable explosion temperature increases. The temperature appears to have reached a somewhat constant value of about 230°C at 40% water content. Indeed, in the limit of pure water, this value is close to the accepted range of the limit of superheat of water [3] at which it homogeneously nucleates. We note in passing that an accurate determination of the limit of superheat of water is an extremely difficult task [4]. Values of 250–300°C have been reported in the literature, while we were also able to obtain a 255°C limit of superheat by using silicone oil as the host fluid. It is conceivable that at elevated temperatures Krytox can dissolve trace amounts of

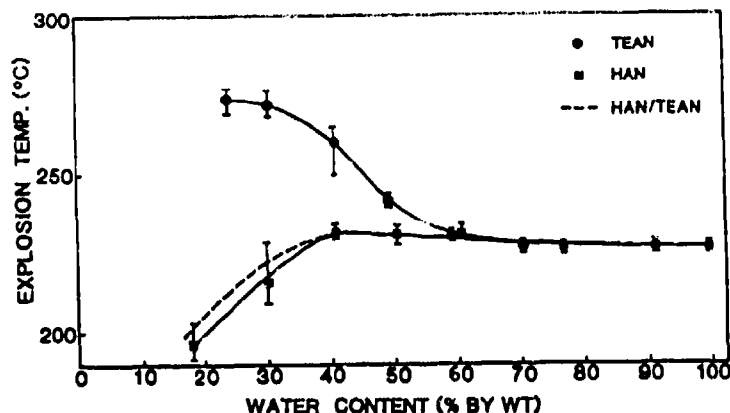


Fig. 3. Explosion temperature of HAN, TEAN, and HAN/TEAN mixtures with various amounts of water addition.

water, thereby causing a lowering of the limit of superheat. Since we are limited to using Krytox in our experiment because of its high density, and since our primary objective is not an accurate determination of the limit of superheat of water, we shall accept the present value as the lower bound of the superheat limit.

Figure 3 shows the corresponding explosion temperature of pure HAN and pure TEAN solutions, with the most probable explosion temperatures of the HAN/TEAN mixtures superimposed. It is seen that the explosion temperature of the HAN solution increases to approach the limit of superheat of water, while that of the TEAN solution decreases to approach it.

The above results provide the following insight into the explosion mechanism of the liquid propellants. It seems that the explosion of LP-1845 is induced by liquid-phase chemical reactions instead of the homogeneous nucleation of water. Furthermore, these reactions are initiated by HAN because its explosion temperature closely follows that of LP-1845. This conclusion agrees with that of Ref. [1]. Figures 2 and 3 further show that as the extent of water dilution is increased, chemical reactivity is continually weakened until the explosion mechanism shifts to that of homogeneous nucleation of water.

A useful piece of information which emerges from the above results is that the reaction temperature of LP-1845 is in the range of 200–230°C, and

therefore is substantially higher than the previously reported values. However, we have not been able to assess the main cause for the lower values reported previously.

3. DROPLET COMBUSTION EXPERIMENTS

A schematic of the droplet combustion apparatus can be found in Refs. [5] and [6]. The experiment basically involves downwardly and coaxially injecting a steady stream of droplets of equal size and spacing into the postcombustion region of a flat flame, whose stoichiometry can be varied to achieve the desired temperature and oxidizer concentration in its downstream flow in which the droplets gasify. The instantaneous droplet image and size can be stroboscopically frozen and photographically recorded, while its corresponding composition can be determined through sampling [5, 6]. Before entering the sampling probe, the droplets are subjected to a gentle blowing of N_2 , which disperses the vapor around the droplets so that only the droplets constitute the collected sample [6]; the dispersed vapor turns out to be negligible. For the present runs the ambient temperature is about 900°C.

Observationally, the droplet combustion phenomena can be described as follows. After injection there exists a period during which the droplet is heated up while its size remains somewhat

constant. Afterward its size decreases steadily. When the ambience is oxidizing, with 21% by mole of oxygen in the present runs, the droplet is surrounded by a bright, diffuse region which is orange-red in color. Such coloration is absent when the ambience is inert.

This quiescent "burning" period is followed by droplet microexplosion. If the initial water content of the propellant is less than about 40%, microexplosion occurs in one violent event. However, if the water content is between 40% and 60%, microexplosion occurs in two stages. At the first stage only very mild disruption was observed, which typically involves the ejection of a few very small microdroplets from the parent droplet whose size is therefore only minimally reduced. This is followed by another quiescent period of gasification until the onset of the second explosion which violently ruptures the droplet. No droplet disruption was observed for water contents higher than 60%.

Figure 4 shows the conventional D^2 - t plot for the LP-1545 propellant in the oxidizing environment, where D is the instantaneous droplet diameter and t is the time. The results quantify the above phenomenological description in that each curve typically consists of an initial flat period of active droplet heating and minimum gasification, which is followed by a period of linear regression in agreement with the D^2 -law, and is eventually

terminated by microexplosion. Figure 5 shows that the droplet behavior in the inert environment is similar to that in the oxidizing environment, not only qualitatively but also quantitatively. For excessively large droplets the burner is not long enough for the droplets to achieve the state of microexplosion.

Figure 6 shows the D^2 - t plot for a high water concentration case, demonstrating the phenomenon of two-staged explosion.

The gasification rates under various situations can be quantified by the gasification rate constant

$$K = -\frac{d}{dt}(D^2)$$

for the period during which the linear behavior holds within the accuracy of the experimental data. In Fig. 7, K is plotted as a function of water content in the propellant for initial droplet sizes around 200 μm . In cases involving two-staged explosion, the K value corresponding to the first linear segment is used; this value is found to be slightly higher than that of the second segment. Figure 7 shows a steady, very gradual increase in K with increasing water content such that at 100% water content the vaporization rate of pure water is recovered. This observed increasing trend is reasonable because water, being the more volatile component as compared with the salts, has a

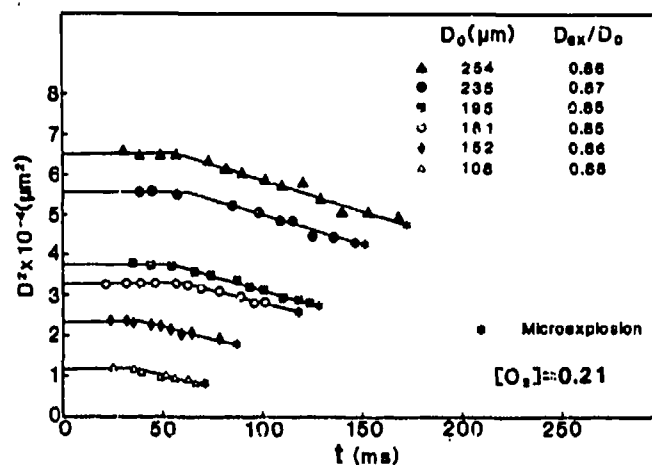


Fig. 4. D^2 - t plot of the gasification history of the LP-1545 propellant droplet in an oxidizing environment with 21% by mole of oxygen.

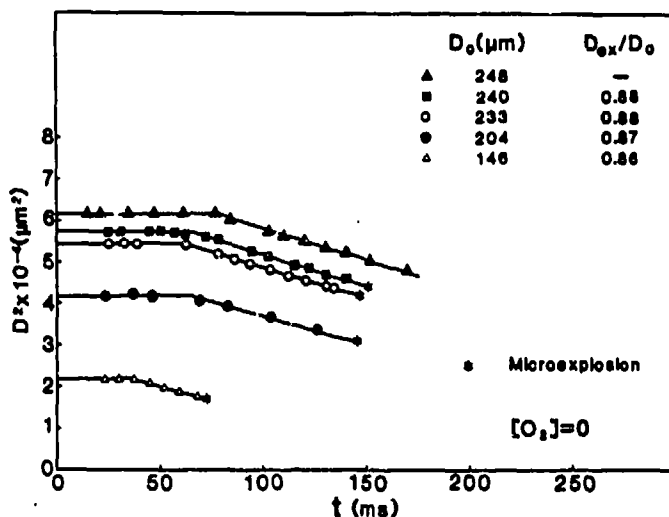


Fig. 5. D^2 - t plot of the gasification history of the 1845 propellant droplet in an inert environment.

higher gasification rate and therefore tends to be preferentially vaporized.

Figure 8 shows the dependence of K on the initial droplet diameter D_0 for the oxidizing environment for the LP-1845 propellant; results for the inert environment are qualitatively as well as quantitatively similar. It is seen that K increases somewhat linearly with D_0 . This is an interesting result because the D^2 -law indicates that K does not depend on D_0 ; indeed such a dependence was not observed for cases with high water content. One possible explanation for the increasing trend is the

potential existence of mild exothermic liquid-phase reactions prior to the onset of microexplosion. These mild reactions generate small amount of heat which can facilitate droplet gasification without distorting the D^2 - t "linear" profile to any observable extent. Since large droplets allow longer reaction times, higher gasification rates can be expected.

We next study the behavior of the diameter D_{ex} at which a droplet microexplodes. First, the tabulated values in Figs. 4 and 5 show the interesting behavior that the normalized explosion

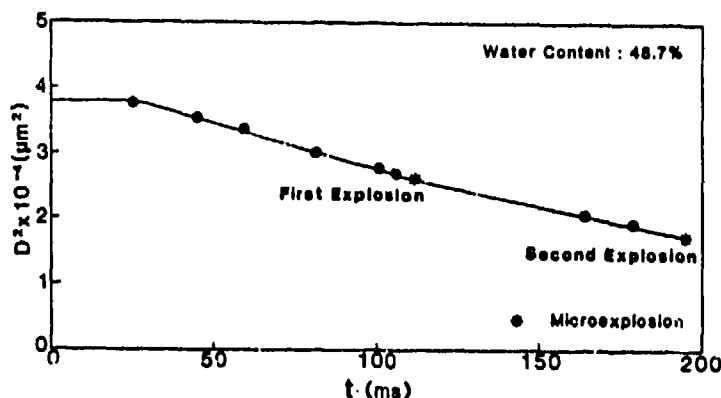


Fig. 6. D^2 - t plot of the gasification history of a highly diluted 1845 propellant droplet, demonstrating the phenomenon of two-staged explosion.

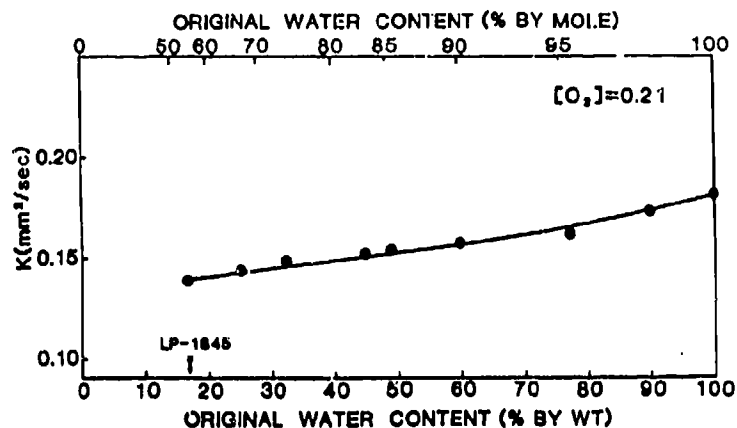


Fig. 7. Dependence of the gasification rate constant K as a function of water content in the propellant droplet.

diameter, (D_{ex}/D_0) , attains an almost constant value of about 0.85–0.88 regardless of D_0 , for both the oxidizing and inert environments. This indicates the possible existence of some critical salt concentrations at explosion, at least for the LP-1845 propellant shown.

Figure 9 shows (D_{ex}/D_0) as a function of water content. In cases involving a two-staged explosion, the D_{ex} values at the second explosion event are used. It is seen that droplet explosion is delayed with increasing water content, as is reasonable to expect because in order to achieve a high enough salt concentration and thereby droplet temperature to induce microexplosion, more water

needs to be vaporized for droplets with higher initial water content. The overall variation, however, is not large. No explosion was observed for water content exceeding 60% as mentioned earlier.

To explore further the possible existence of a critical salt concentration and thereby density at microexplosion, we have sampled and determined the liquid density just prior to the onset of microexplosion. The droplet sampling procedure follows that of Ref. [6]. To ensure that the collected propellant in the sampling vial is not contaminated by condensation of the water vapor from the hot environment, simulated sampling

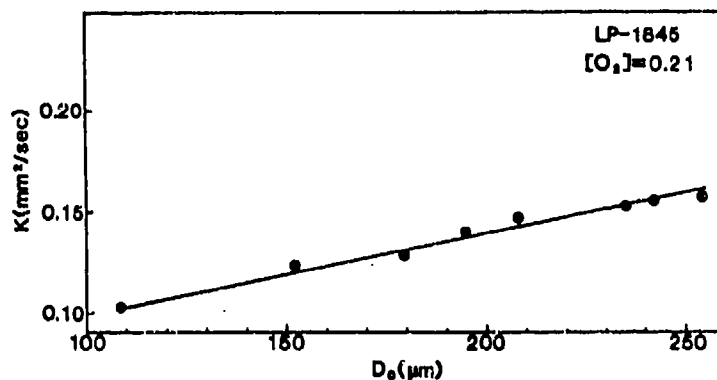


Fig. 8. Dependence of the droplet gasification rate constant K as a function of initial droplet diameter for the 1845 propellant in the oxidizing environment.

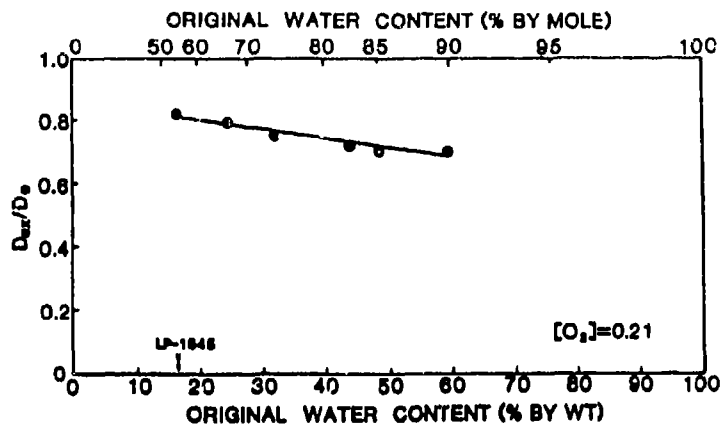


Fig. 9. Dependence of the normalized droplet explosion size, D_m/D_0 , as a function of water content in the propellant droplet.

runs without the droplet stream were conducted to determine the amount of water vapor that was collected in a typical run. The results show that this amount is less than 0.5% of the total droplet sample collected and is therefore negligible.

The propellant density at microexplosion has thus been determined, at 25°C, for initial droplet diameters ranging from about 200 to 750 μm , and for initial water content over the range shown in Fig. 10. It is found that, regardless of the initial droplet size and water content, the propellant attains a constant density of about 1.5 g/cm^3 when microexplosion occurs.

The above results on the critical explosion density can be interpreted as follows. After the initiation of droplet gasification, water is preferentially depleted as gasification proceeds. This leads to a steady increase in the salt concentration and thereby in the droplet temperature for equilibrium vaporization. It is then possible that when the droplet temperature reaches a critical value, which corresponds to a critical salt concentration and therefore liquid density, the rate of liquid-phase reaction is greatly accelerated in such a way that internal gasification is spontaneously initiated.

If we next extrapolate the curve representing the

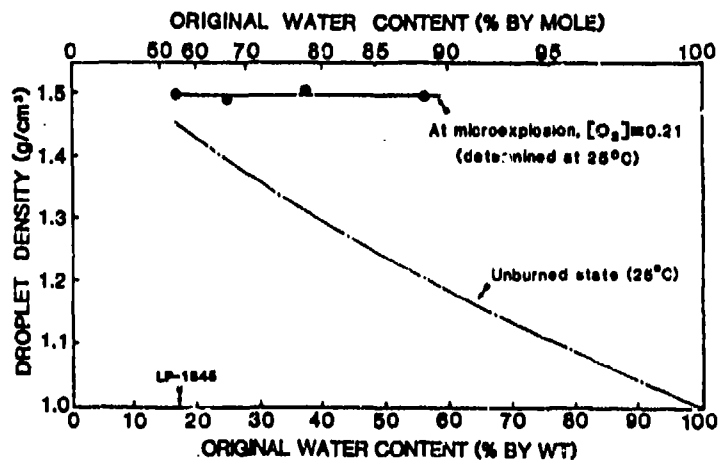


Fig. 10. Density of the diluted propellant just prior to the onset of microexplosion, for various amounts of water dilution.

density of the unburnt propellant to 1.5 g/cm^3 (Fig. 10), a value of about 12% for the original water content is obtained. It can then be suggested that droplets of liquid propellants with water contents of 12% or less can conceivably achieve instant microexplosion once droplet heating is over. In light of this possibility, we have attempted to increase the salt concentration of the available LP-1845 by placing it under vacuum and therefore vaporizing off some of its water content. The sample so obtained indeed exhibited a lower range of explosion temperatures, between 170 and 205°C, with the most probable value of 190°C. However, we were not successful in obtaining reliable data on droplet gasification and microexplosion because of the difficulty in generating droplets from the condensed sample which is highly viscous.

4. DISCUSSION

The present results yield the following insight into the combustion and microexplosion characteristics of droplets of liquid propellants. First, results on the droplet explosion temperature, which is substantially higher than previously reported values, indicate that propellant explosion is likely induced by liquid-phase reaction for salt concentrations less than 30–40% of water, and by the homogeneous nucleation of water for higher water concentrations. Furthermore, HAN is the salt component that initiates the liquid-phase reaction.

Concerning the droplet gasification, the following approximate mechanism can be suggested. Upon exposure to the hot environment, whether it is oxidizing or inert, the droplet is first heated up and suffers very little mass loss. The period of heating depends on the droplet size while the extent of heating depends on the salt concentration. Thus the higher the salt concentration, the higher the droplet temperature will reach before this period of active droplet heating is over.

Active droplet gasification follows active droplet heating. The result that the gasification rate constants of the propellants (Fig. 7) are close to that of pure water suggests that water is the dominant gasifying species. The salts, however,

are nevertheless also gasified to a certain extent because of the presence of the orange coloration surrounding the droplet when the environment is oxidizing. Mild liquid-phase reactions could also be taking place because of the somewhat substantial dependence of K on the initial droplet size (Fig. 8).

The preferential gasification of water will lead to the gradual concentration of the salt in the droplet. The efficiency and extent with which salt is concentrated depend on the diffusional resistance experienced by the salt in the solution. The present data seem to suggest that the diffusional resistance may not be too strong, for two reasons. First, if diffusional resistance were strong, the gasification rate would have a much stronger dependence on the salt concentration, contrary to the observation. Second, the gasification rates of the LP droplets are between 0.14 and 0.18 mm^2/s , which are substantially lower than the value of about 1 mm^2/s for miscible hydrocarbon droplets. These lower gasification rates allow a longer time for the salt to diffuse. Furthermore, recent experimental results [6] have shown that diffusional resistance is not overwhelmingly strong even for miscible multicomponent droplets.

With salt being continuously concentrated, a critical concentration corresponding to an average droplet density of 1.5 g/cm^3 can be eventually reached, at which liquid-phase reaction is rapidly accelerated to cause droplet microexplosion. For mixtures with high initial water contents, it is possible that this critical density cannot be reached because during droplet gasification salt is still being depleted from the droplet composition to a certain extent. For these mixtures microexplosion does not occur.

In order to explore the viability of the above concepts, it is necessary to determine the temporal variation of the droplet composition. Since conventional analytical chemical techniques fail because of the corrosive nature of the salts, we are currently exploring special techniques for performing such an analysis.

Finally, it is also necessary to mention that in the realistic environment of the gun interior the pressure is excessively high while the environment

is also rich in water vapor. It is reasonable to expect that significant modifications in the droplet gasification and microexplosion behavior will result when these effects are accounted for.

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**COMBUSTION AND MICROEXPLOSION OF HAN-BASED
LIQUID GUN PROPELLANTS UNDER ELEVATED PRESSURES***

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Abstract

The combustion of freely falling liquid propellant droplets in a high temperature, elevated pressure environment up to about four atmospheres has been studied. The influences of ambient pressure, ambient temperature, initial propellant water concentration, and initial droplet size on the droplet combustion rate and the state of microexplosion have been systematically investigated. Results show that with increasing pressure and temperature, the droplet gasification rate increases while the state of microexplosion is also advanced to the very early stages in the droplet lifetime. The opposite holds with increased propellant water content.

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I. INTRODUCTION

Presently there exists much interest in the use of a class of liquid propellants (LP) for the launching of gun ordnances [1]. These propellants are composed of salts of hydroxylammonium nitrate (HAN) and an aliphatic ammonium nitrate (AAN) dissolved in water. Since HAN is oxygen rich based on N_2-H_2O stoichiometry while AAN is oxygen deficient, they are usually mixed in stoichiometric proportions for maximum propellant energy density. The AAN which is being widely studied at present is triethanolammonium nitrate (TEAN) while the specific LP being tested is coded 1845, which consists of 63.2% HAN, 20% TEAN, and 16.8% water, all by weight. This LP has a heating value of about 1 kJ/g and a calculated adiabatic flame temperature of 2285K. This is the LP adopted for most of the tests conducted in the present study.

Very little is known about the combustion properties of these propellants, although some useful information has been recently reported [2-4]. Specifically, in Ref. 2 it was determined, for atmospheric pressure conditions, that the liquid-phase reaction of LP-1845 is initiated around 200 to 230°C, that HAN is the component which initiates this reaction, that in practical situations this temperature range can be lower because of the preferential gasification of water and thereby concentration of the salts prior to the onset of reaction, and that there seems to exist a critical salt concentration at which reaction occurs spontaneously. In Ref. 3 the flame propagation process within the LP was studied under high pressure situations, from 68 to 300 atm. The results again demonstrate that it is HAN which initiates the reaction. In Ref. 4 the thermodynamic critical parameters of the LP were estimated. The results show that the critical pressure can be very high such that the LP may not attain criticality during most of the burning time within the ultra-high pressure environment of the gun chamber.

In the present investigation we extend the droplet combustion work of Ref. 2 to elevated pressure environments. The work is primarily motivated by the recognition that liquid-phase reaction is a crucial element of LP combustion, and that its initiation and intensity can be greatly affected by the liquid temperature. Since thermodynamically, the attainable liquid temperature increases with increasing pressure, it is then reasonable to expect that the liquid-phase reaction can be correspondingly facilitated by increasing the system pressure. We shall demonstrate subsequently that this concept of pressure-enhancement is indeed viable.

The experimental methodology is presented in the next section, which is followed by discussion of the experimental results.

II. EXPERIMENTAL METHODOLOGY

A steady-flow combustion chamber is used to study the gasification and microexplosion of freely-falling LP droplets. A schematic of the apparatus is shown in Fig. 1. Basically, the experiment involves downwardly injecting a steady stream of monodispersed and equally-spaced LP droplets into the hot post-combustion zone of a flat flame, and observing the subsequent combustion event by freezing the droplet image with stroboscopic back lighting. A solid-state CCD camera is mounted on a zoom microscope for droplet imaging. The camera signal is transmitted to a video tape recorder and a high resolution monitor, allowing a convenient means for focusing and recording. The overall magnification from the actual droplet size to the video monitor is about 275X, and the measurement uncertainty is less than two percent of a typical 200 μm droplet.

The pressure in the chamber is accurately controlled by an exhaust gas valve. Accurate flow measurements of all gases to the chamber is provided by

sonic orifice control valves such that the ambient temperature and species concentrations can be specified within practical limits. Two fuels, methane and carbon monoxide, have been used to produce the desired environment, although the results to be presented do not seem to have any noticeable dependence on which gas is used.

The temperature along the centerline of the chamber typically assumes the profile as shown in Fig. 2. The initial section of low temperature is due to mixing of the hot ambient gas with the purge gas from the droplet injector. After attaining a maximum, the gas temperature gradually decreases due to heat loss. The decrease, however, is mild. All of the steady droplet gasification data were taken with a temperature variation of less than 50K; in most cases the variation is less than 25K. The gas temperature reported here is the thermocouple measured value at 6 cm from the burner (Fig. 2).

III. RESULTS AND DISCUSSIONS

For a given experiment, the independent system parameters which turned out to be important are the ambient pressure (p), ambient temperature (T), initial droplet size (D_0), and initial water content in the LP. With these parameters specified, we measure the droplet diameter (D) as a function of time (t), especially its value just prior to the state of microexplosion (D_{ex}).

Figure 3 is a typical D^2 - t plot in accordance with the D^2 -Law of droplet gasification. It is seen that after the initial droplet heating period D^2 varies fairly linearly with time. For higher pressures the data bends down slightly, indicating a gradual increase in the gasification rate. In all cases shown droplet gasification was terminated in microexplosion.

From the D^2 - t data a gasification rate constant K can be approximately

defined as the negative of the slope of the best-fit straight line passing through the data in the active gasification regime. Figure 4 shows K as a function of the ambient temperature T for $p = 1$ atm and $D_0 = 185 \mu\text{m}$. It is seen that the droplet burning rate increases quite significantly with T . These are two causes for such an increase. The first is simply the increase in the heat transfer rate from a hotter ambience to the droplet. The second is the possibility that some mild liquid-phase reactions exist within the droplet. Thus with increasing gas temperature the rates of these reactions and the associated heat release also increase because of the higher droplet temperature. This then leads to a faster droplet gasification rate.

In order to distinguish which of these two possibilities is the major contributing factor to the enhanced burning rate, we have also determined the variation of K with T for water only; in this case liquid-phase reaction is absent such that the variation can only be caused by enhanced heat transfer. Figure 5 shows that for pure water K increases only slightly with increasing T , therefore indicating that the sensitive response of the LP droplet to ambient temperature variation is caused by liquid-phase reactions.

The present result that mild liquid-phase reactions exist in the droplet interior over an extended period of time prior to the onset of microexplosion also confirms our previous data [2] which show that K increases with D_0 (Fig. 6). This is because K should be a constant for a non-reacting droplet undergoing steady gasification in a hot ambience. Thus the positive dependence on D_0 is a manifestation of the effects of increased volumetric heat release and longer lifetime (and thereby longer reaction time) associated with larger droplets.

Figure 7 shows the dependence of K on the ambient pressure p . It is seen that the dependence is again very strong, with the similar sensitivity as the

dependence on T shown in Fig. 5. It is reasonable to suggest that the increase in K is caused by the enhanced liquid-phase reaction because of the increase in the droplet temperature with increasing pressure.

We now present results on droplet microexplosion. The efficiency of microexplosion is quantified by D_{ex}/D_0 such that a value near one indicates early microexplosion and thereby maximum effect on facilitating droplet gasification.

Figure 8 shows that increasing ambient temperature advances the occurrence of microexplosion. This is in agreement with the result implied by Fig. 4 that the droplet temperature increases with T . Thus with increasing droplet temperature not only the mild liquid-phase reactions are facilitated to cause a higher K , but the enhanced mild reactions also lead to an earlier attainment of the chemical runaway situation manifested by microexplosion.

Figure 9 shows that (D_{ex}/D_0) increases with increasing ambient pressure p . This agrees with our earlier anticipation that increasing pressure increases the attainable temperature of the droplet, and consequently advances the state of microexplosion.

Figure 10 shows that microexplosion is delayed with increasing water content. This is reasonable because more water needs to be depleted from an LP with a higher water content in order for the salt to be sufficiently concentrated for chemical runaway to take place.

IV. CONCLUDING REMARKS

The effect of ambient temperature and pressure on the gasification rate can be interpreted as follows. For increasing pressure, the boiling point rises, and thus the droplet temperature during the surface regression period is higher. The data shows that this leads to faster regression rates. For

increasing temperature, the surface regression rate for the LP rises more sharply than for pure water. This suggests that mild liquid-phase reactions occur, and occur more rapidly as the temperature rises.

Increased reaction rates lead to a faster heat release within the droplet, and chemical runaway will occur, resulting in microexplosion. Increased temperature and pressure expediate this process, but increased water content lowers the droplet temperature during much of the gasification and hence, lowers the chemical reaction rates.

Acknowledgements

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Figure Captions

- Figure 1 Schematic of elevated-pressure droplet combustion apparatus.
- Figure 2 Centerline temperature profile in combustion chamber.
- Figure 3 D^2 -t plot for LP1845 for three different pressures.
- Figure 4 Gasification rate constant for LP1845 as a function of ambient temperature at 1 atm.
- Figure 5 Gasification rate constant for LP1845 as a function of ambient pressure at 1000K.
- Figure 6 Gasification rate constant for LP1845 as a function of initial droplet diameter at 1 atm and 1150K.
- Figure 7 Gasification rate constant for water as a function of temperature at 1 atm.
- Figure 8 Microexplosion diameter of LP1845 as a function of temperature for 1 atm.
- Figure 9 Microexplosion diameter of LP1845 as a function of pressure at 1000K and 1100K.
- Figure 10 Microexplosion diameter of LP1845 with water dilution as a function of pressure at 1000K.

ELEVATED PRESSURE DROPLET COMBUSTION APPARATUS

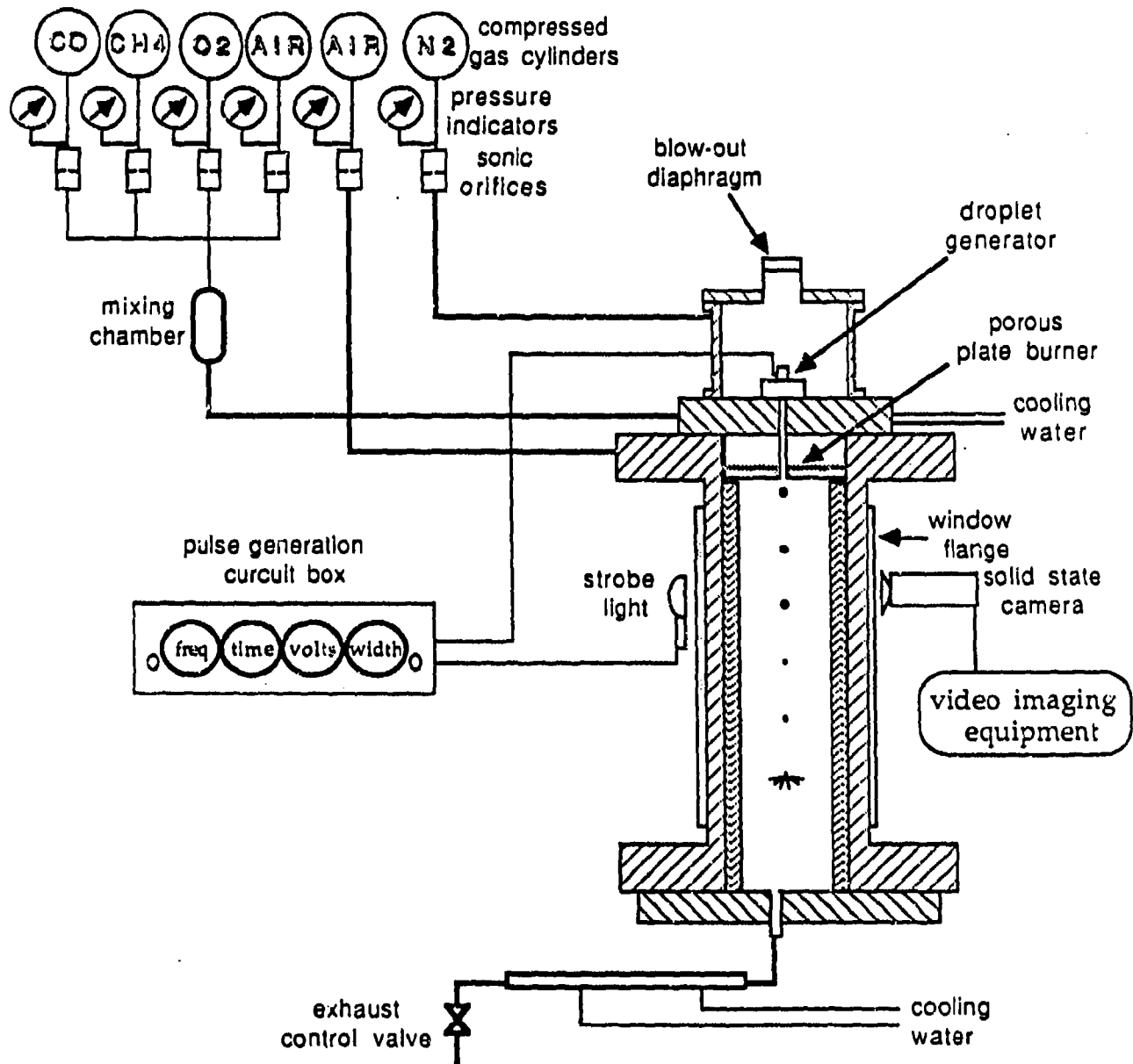
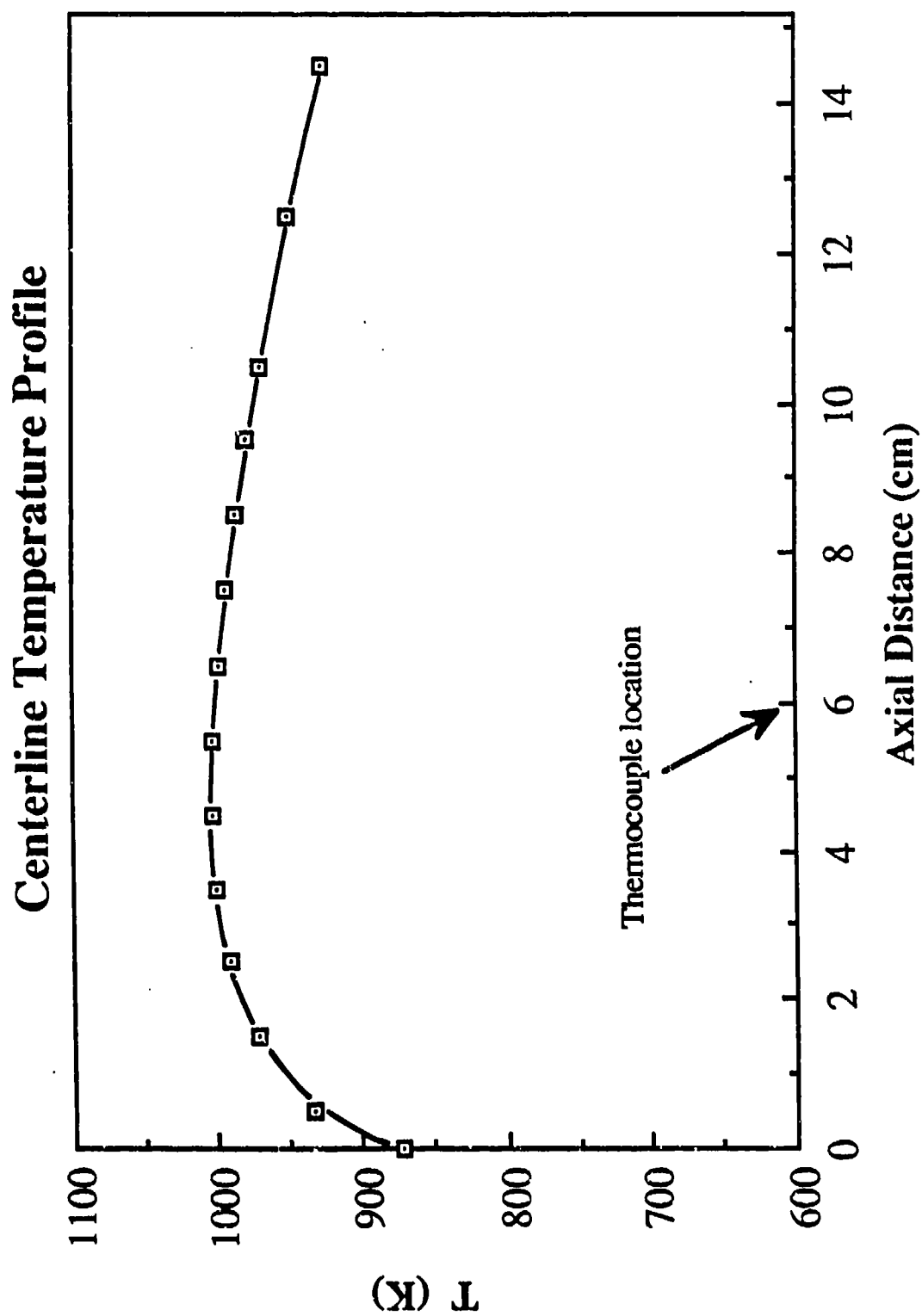


Figure 1

Figure 2

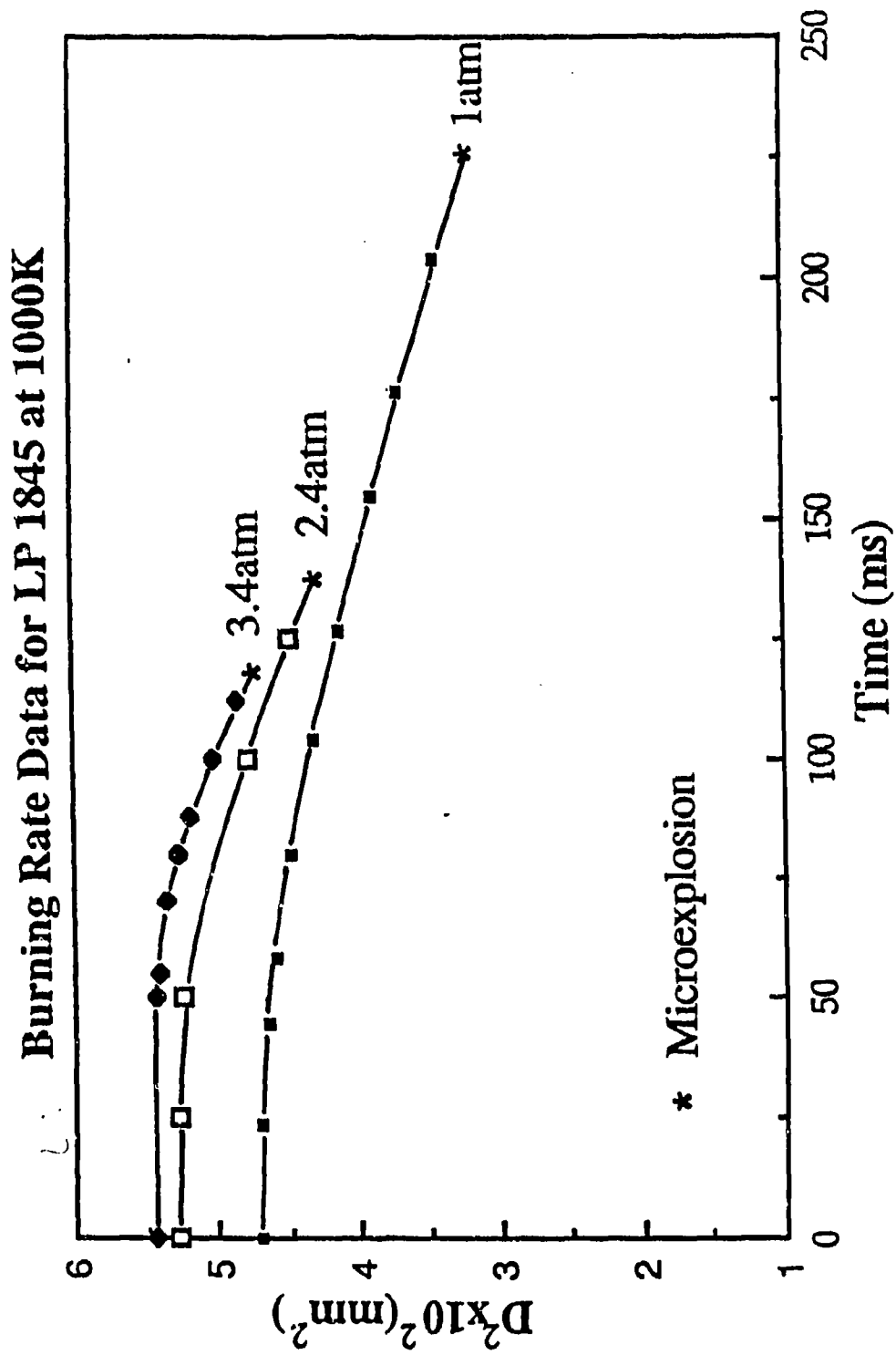


Figure 3

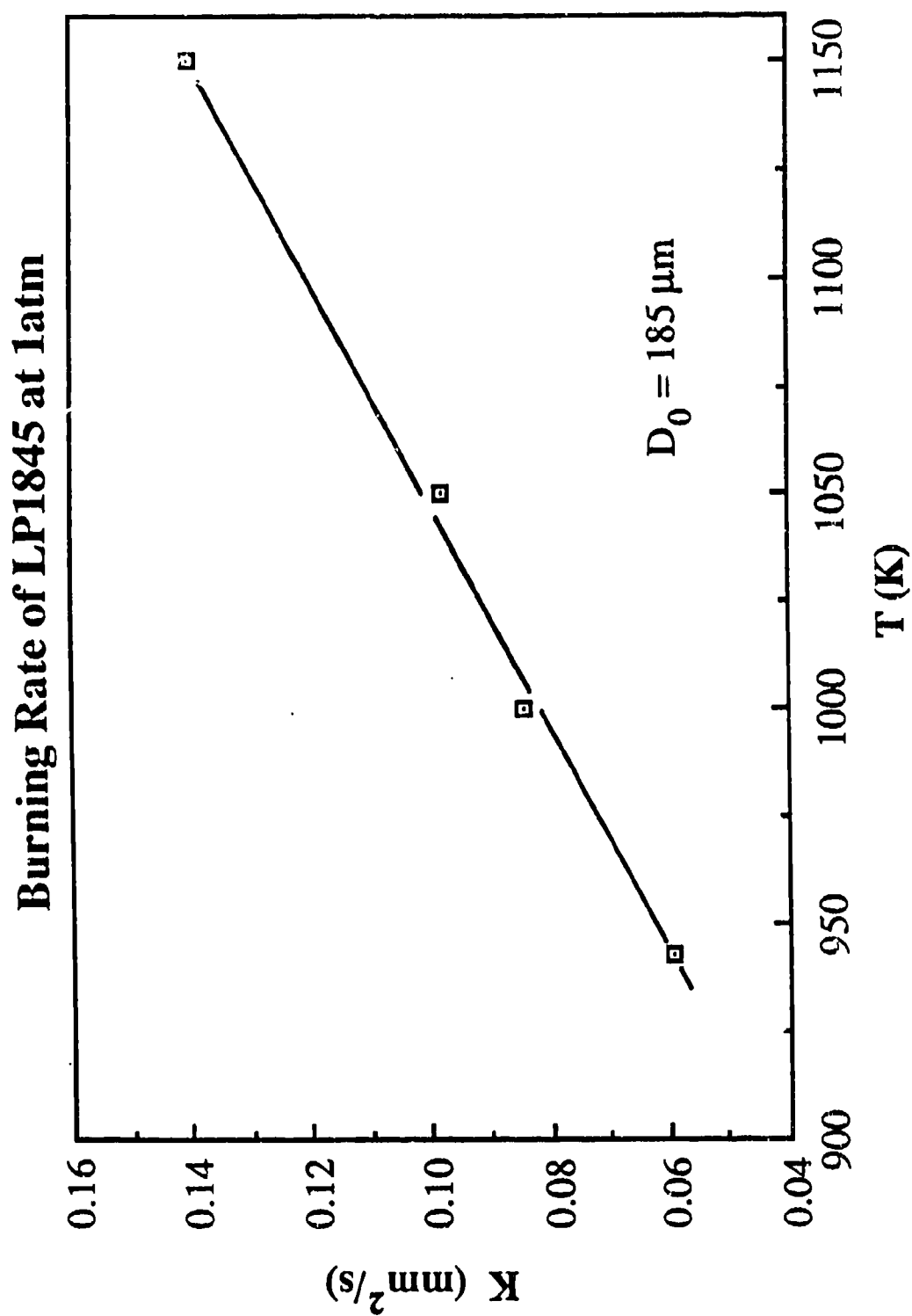


Figure 4

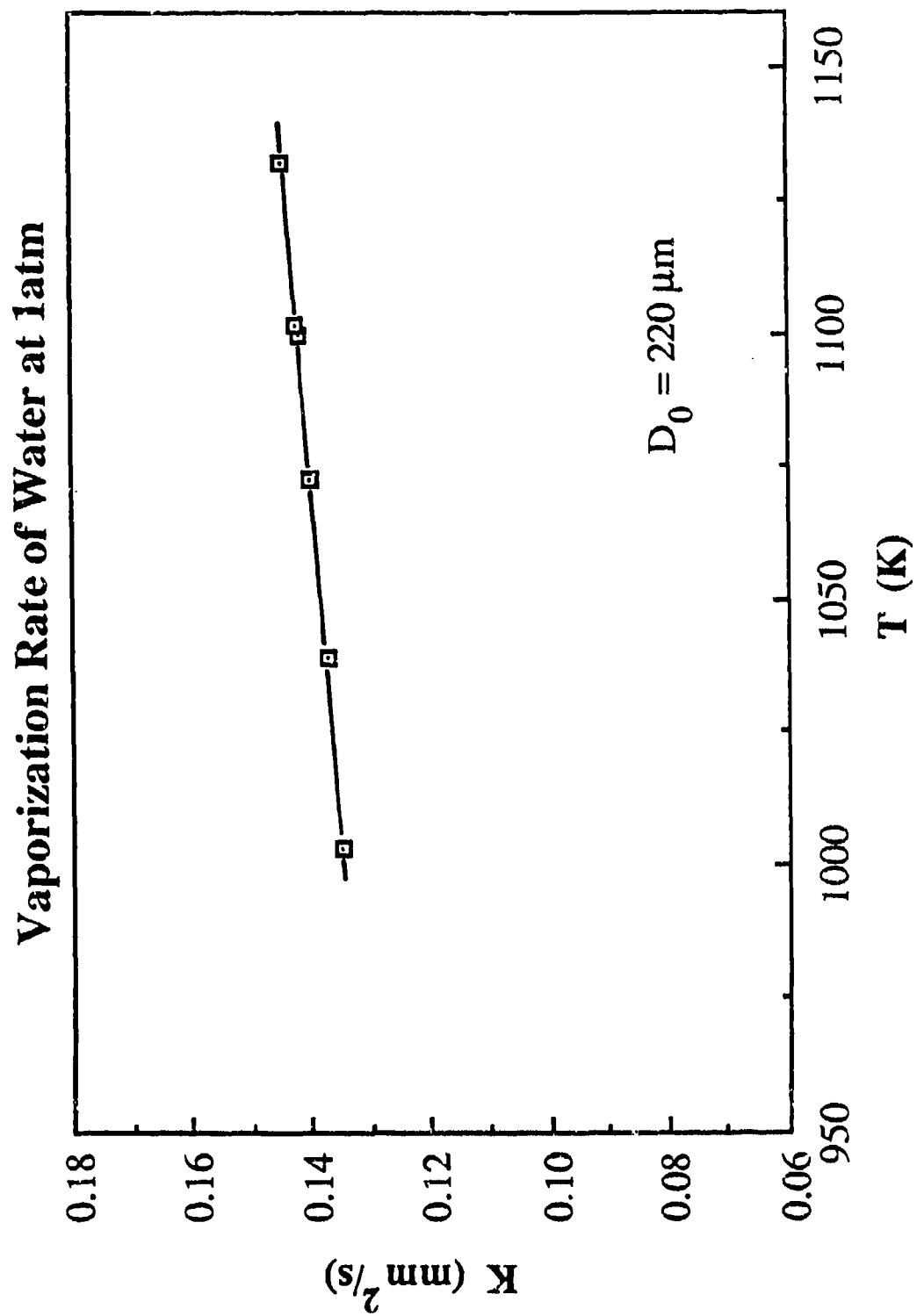


Figure 5

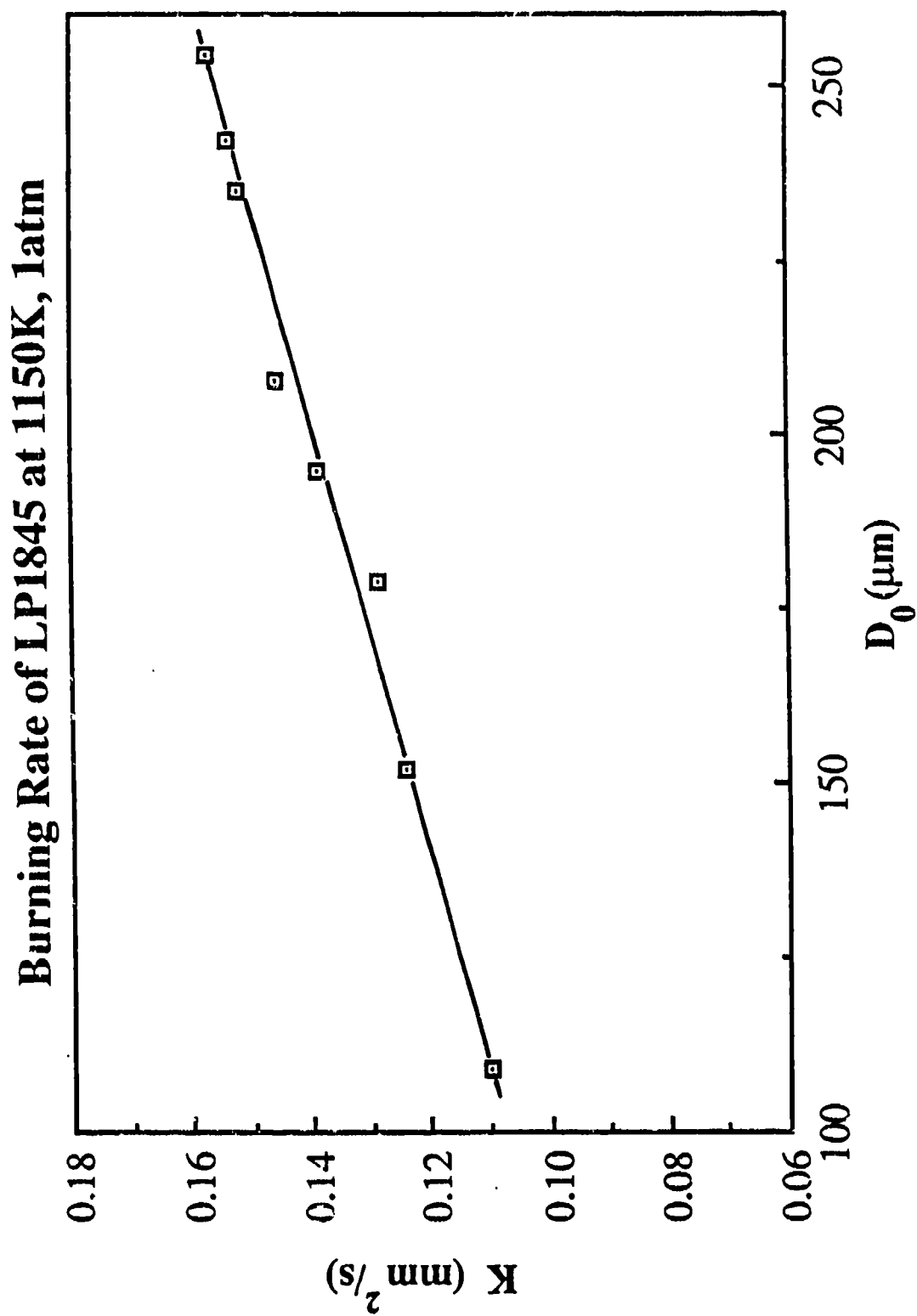
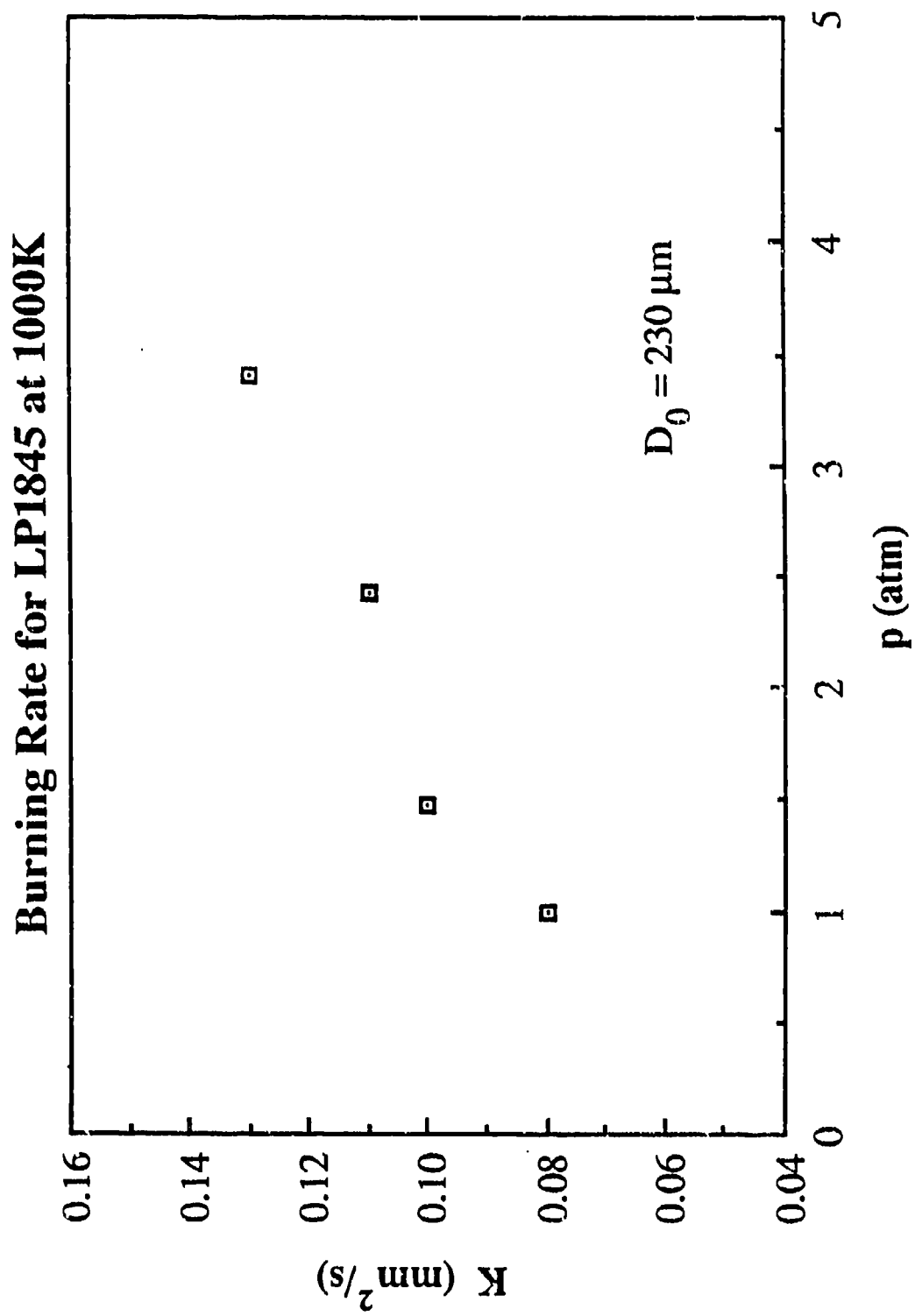
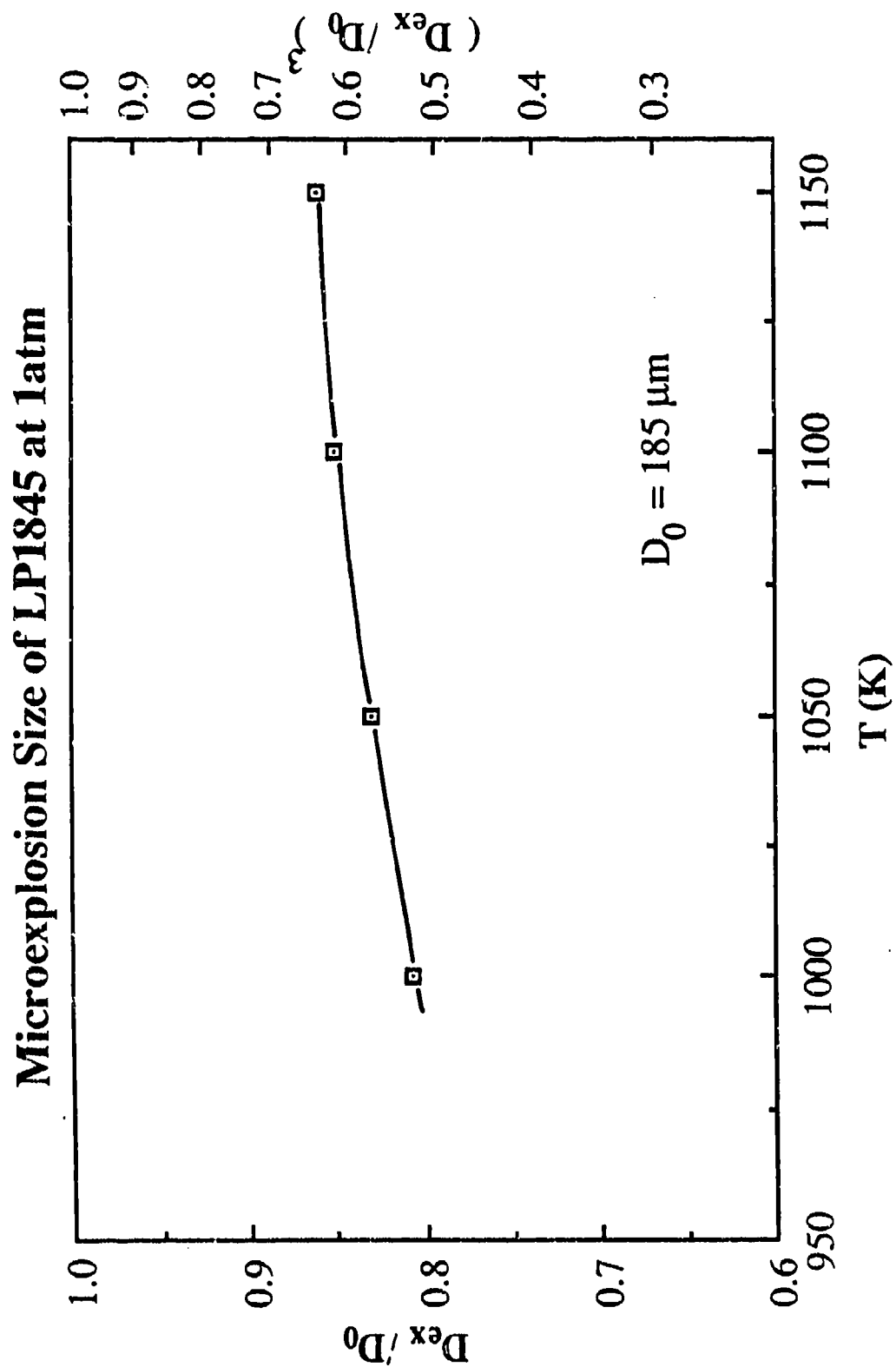


Figure 6

Figure 7

Figure 8

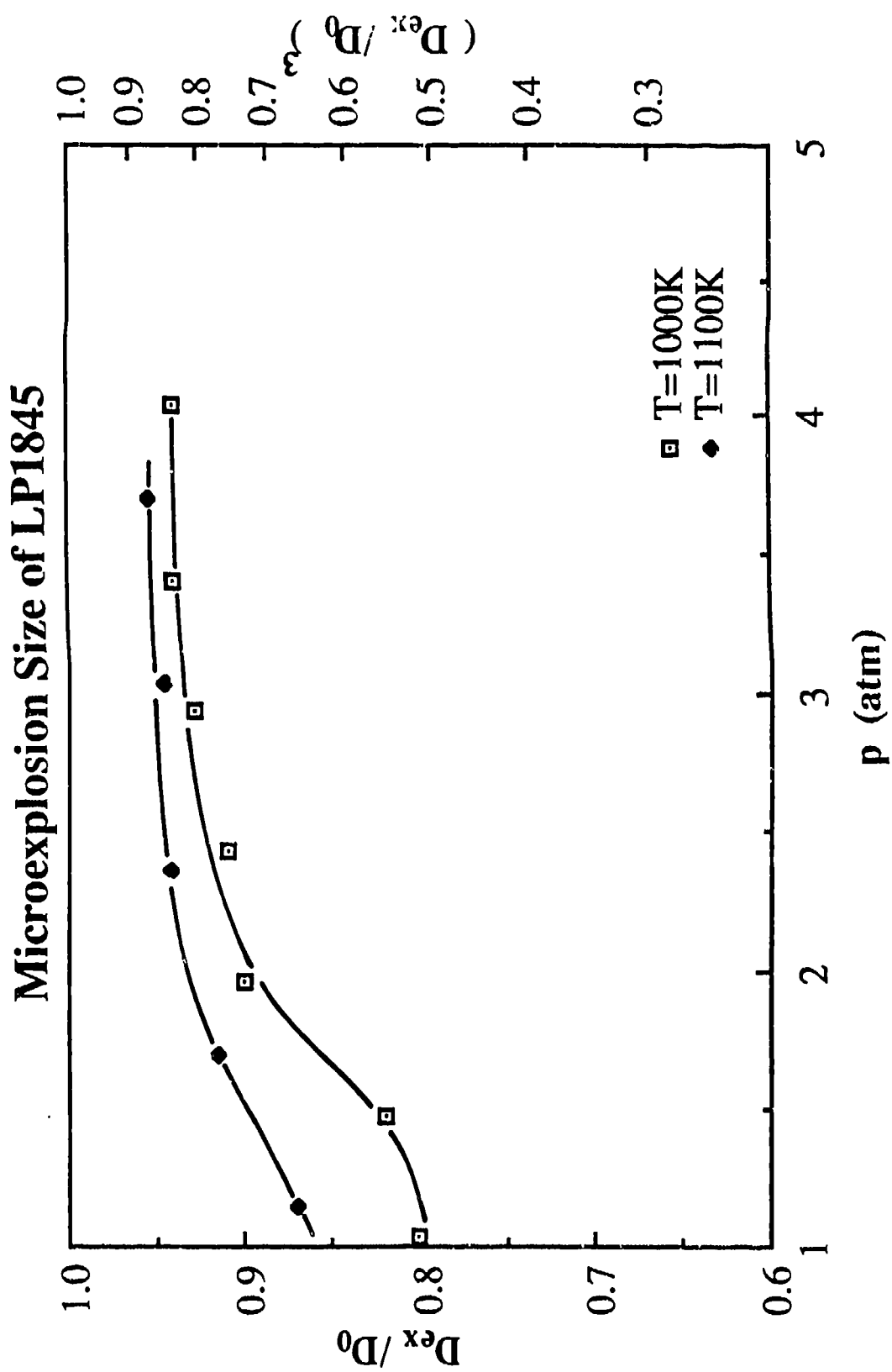


Figure 9

Microexplosion of LP with Water Addition at 1000K

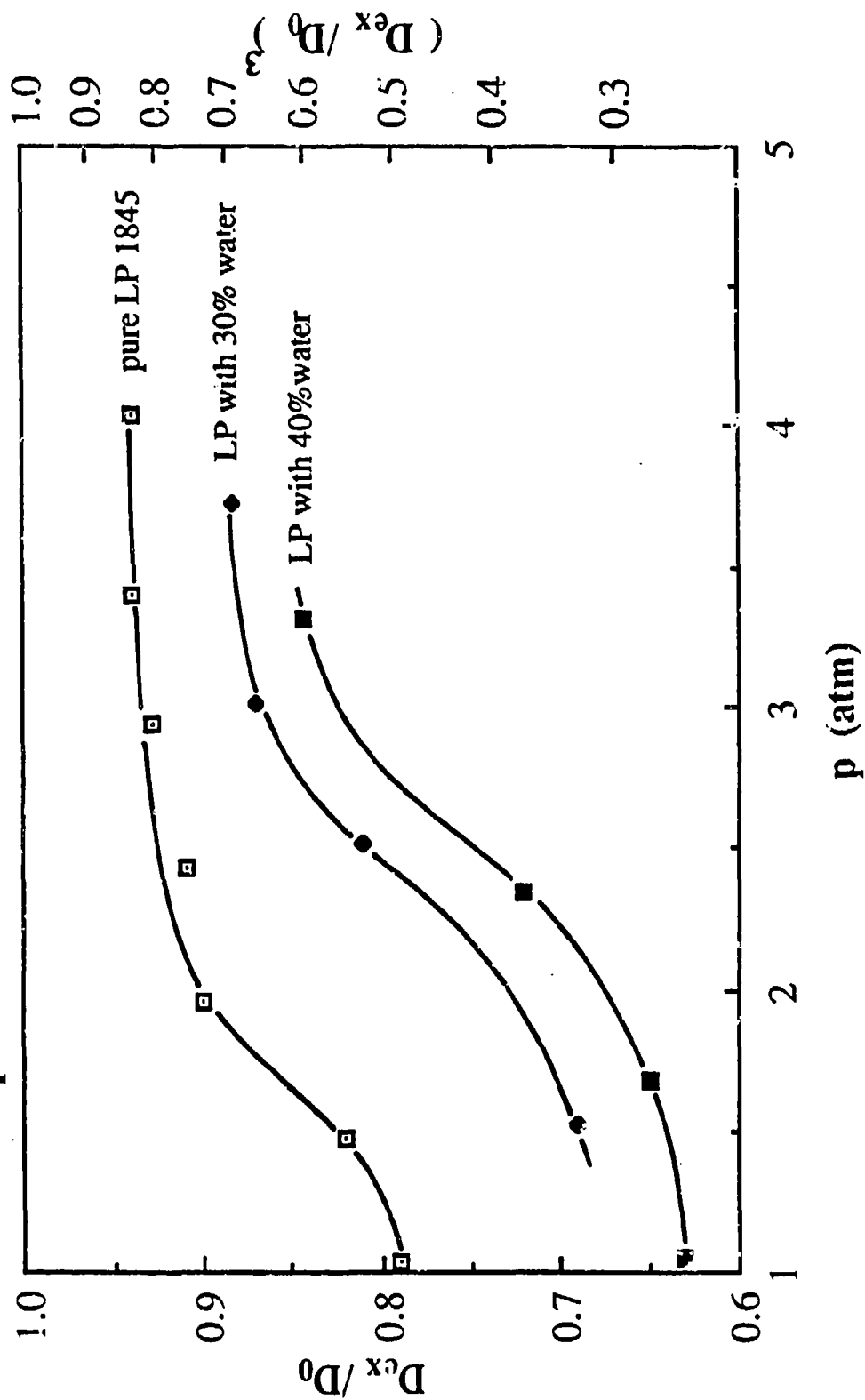


Figure i0